

SOLID ELECTROLYTES USING ABSORBENT
AND METHODS FOR PREPARING THEM

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Technical Field

The present invention relates to an electrolyte film usable in rechargeable cells. More particularly, it relates to a provision of pathways for ions mobile between a cathode and an anode during repeated charge and discharge of rechargeable cells by introducing liquid components and lithium salts (hereinafter, both are referred to as "liquid electrolytes") to an electrolyte film containing an absorbent.

Electrochemical cells include three essential components, i.e., cathode, anode and electrolyte. Examples of materials for said anode are typically compounds in which lithium metal or lithium ions can be intercalated, preferably carbon and polymer materials. Examples of materials for said cathode are typically materials in which lithium ions can be intercalated. For example, oxide compounds or polymer materials such as lithium cobalt oxide (Li_xCoO_2), lithium nickel oxide (Li_xNiO_2), lithium nickel cobalt oxide ($\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$), spinel type lithium manganese oxide ($\text{Li}_x\text{Mn}_2\text{O}_4$) and manganese dioxide (MnO_2) can be used. The introduction of a liquid electrolyte to said electrolyte film can lead to the formation of an ion conductive matrix.

Background Art

Electrochemical cells using polymer electrolytes have some
5 advantages over ones using liquid electrolytes in that i) they have less
leakage risk of liquid; ii) they have excellent electrochemical stability,
which makes it possible to manufacture various types of cells; and iii)
they make the automation of the manufacturing process easy.

10 Since the fact that polymers such as polyoxyethylene may have
metal ion conductivity in the case that they contain polar heterologous
atoms capable of electric interaction with metal ions was found,
research on ion conductive polymers, i.e., polymer electrolytes has
been actively conducted. However, since pure polymers such as
15 polyoxyethylene have very low ionic conductivity of 10^{-8} S/cm or so at
room temperature, they have a demerit in that they should be
approached to the temperature of approximately 100°C in order to
show ionic conductivity of approximately 10^{-4} S/cm applicable to
electrochemical cells. For this reason, the main stream of the research
20 on polymer electrolytes was concentrated on the improvement of
conductivity.

As the fact that the conduction of ion in polymer electrolytes
requires movement of polymer chains was found, attempts to improve
25 conductivity of ions have been carried out in a direction of increasing
the flexibility of polymer chains. Blonsky *et al* proposed a method for
manufacturing an electrolyte having increased conductivity of 10^{-5}

S/cm by introducing phosphazene linkages to the main chain of the polymers (*J. Am. Chem. Soc.*, 106, 6854 (1984)). However, said electrolyte has lower conductivity and poor mechanical strength.

5 Alternatively, in order to decrease the crystallinity of polymers, various attempts such as modifying the structure of polymers or adding inorganic materials to polymers have been conducted. However, pure polymer electrolytes consisting of polymers and metal salts (not containing liquid electrolytes) still do not have sufficient conductivity.

10 On the contrary, gel-type electrolytes disclosed in US Patent 5,219,679 contain liquid electrolytes in their polymer backbones, and thus demonstrate conductivity close to that of liquid electrolytes while having properties of polymers in their mechanical properties,
15 suggesting the possibility of commercialization to rechargeable battery. Namely, the electrochemical cell of said patent doesn't need a particular activation step of adding a liquid electrolyte, but contains some amount of liquid electrolytes which were incorporated during the manufacture of the polymer electrolytes (a mixture of polymer solution
20 and liquid electrolyte was subjected to casting). However, the electrolytes in the US Patent No. 5,219,679 have problems in that they contain polymers such as polyacrylonitrile which are reactive to lithium metal, and thus reaction products between electrolytes and lithium electrode come to be accumulated during the storage and use period of
25 the cell, resulting in a constant increase in interfacial resistance.

Meanwhile, Scrosati *et al* manufactured gel-type polymer electrolytes using polymethylmethacrylate having low reactivity with lithium metal (*Electrochim. Acta*, 140, 991 (1995)). These electrolytes, which use polymethylmethacrylate as a polymer component, have little reactivity with the surface of lithium, and thus have a merit in that the resistance increase phenomenon on the surface of electrode during the storage is insignificant. However, they also have demerits in that they have poor mechanical strength and thus the content of the polymers should be increased to accomplish strength sufficient to form a film, which in turn decreases the conductivity down to 10^{-4} S/cm. In addition, since the gel-type electrolytes contain a large amount of liquid components, it is inevitable that the evaporation of the liquid components on the surface of the electrolytes will occur. For this reason, there have been some risks of causing composition changes due to the loss of liquid components during the storage, which leads to the decrease in conductivity. In addition, this method has a demerit of necessitating a dehumidifying atmosphere wherein moisture is removed to the utmost since lithium salts contained in the liquid electrolytes react and decompose with moisture in the air.

US Patent No. 5,296,318 and 5,418,091 proposed a hybrid polymer electrolyte system to compensate for the said problems. This hybrid polymer electrolyte can minimize the moisture effect on the process of manufacturing electrolytes by adding the liquid electrolytes susceptible to the effect of moisture prior to the packaging of battery, while taking advantage of the merits of gel-type polymer electrolytes (the gel-type polymer electrolytes contain a large amount of liquid

electrolytes and thus the conduction of lithium ion proceeds via liquid phase, thereby having similar conductivity to that of liquid electrolytes). However, since the liquid electrolytes are added after electrolyte film is prepared, it is necessary for the inside of the electrolyte film to have sites capable of absorbing liquid components therein or driving force making the liquid component possible to be penetrated thereinto. To this end, dibutyl phthalate is added as a plasticizer in the step of preparing electrolyte film, and after the assembly of cell is complete, the plasticizer is extracted by the use of an organic solvent such as alcohol or ether to form sites for liquid component being absorbed. However, due to the procedure of extracting dibutyl phthalate utilizing a chemical reaction, the methods have fatal demerits that the reproducibility is low, the manufacturing yield is reduced, and the automation for mass production is difficult.

Disclosure of Invention

The present invention aims to solve the above-mentioned problems of said prior art at a stroke by adding an absorbent capable of absorbing liquid electrolytes to a polymer matrix to form a solid electrolyte film, and after the assembly of the battery, introducing a liquid electrolyte to the activation procedure of the battery.

The present invention also aims to develop rechargeable cells having excellent performances by the use of such solid electrolytes.

The term "electrolyte film" used in the specification refers to an electrolyte film that is dried condition and does not contain any liquid electrolytes. The term "solid electrolytes" used in the specification means said electrolyte film having ionic conductivity by incorporating liquid electrolytes thereto. Although the solid electrolytes are not in a complete solid state since they contain liquid electrolytes, they are called "solid electrolytes" in order to be distinguished from the liquid electrolytes and because the basic backbone of solid electrolytes starts from the electrolyte film at a solid state. In addition, the term "absorbent" used in the specification means materials capable of absorbing liquid electrolytes or of increasing the ability of the solid electrolytes absorbing liquid electrolytes.

The process for assembling batteries refers to binding a cathode and an anode, which are separately prepared, with an interposed electrolyte film in the manner of laminating, pressing or winding. When the electrolyte film is prepared by one of the said methods, liquid electrolytes are added after the assembly of battery, which can minimize the restriction on dehumidifying atmosphere in the process. Furthermore, according to the present method, the sites capable of absorbing liquid electrolytes are already formed in the course of manufacturing the electrolyte film and thus there is no need for the procedure of extracting a plasticizer. Therefore, the method has some advantages in that it simplifies the process, which not only reduces the production cost but also makes the automation process easy and improves the yield.

The solid electrolytes according to the present invention comprise an absorbent capable of absorbing liquid electrolytes, polymer binders and ion conductive liquid electrolytes. The solid electrolytes according to the present invention have lithium ionic conductivity of more than 10^{-4} S/cm at room temperature.

Examples of absorbents capable of absorbing liquids can be largely divided into absorbents capable of absorbing water and absorbents capable of absorbing oil. Absorbents having excellent water absorption ability can be mostly used in diapers or sanitary napkins. Oil absorbents can be used to remove petroleum leaked from ocean or factories or to remove organic solvents from laboratories. The absorbents used in the present invention are porous polymers or inorganic materials. Said porous polymers are polypropylene or polyethylene to which porosity is introduced by means of net type polymer wherein bulky functional groups are introduced to branched chains or by means of adjusting the parameters of the process according to the present invention. Natural polymers such as pulp, cellulose and cork may also be used.

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As absorbents according to the present invention, any materials in the form of powder that are capable of increasing water absorption ability of liquid electrolytes can be used. Preferably, it is possible to use polymer particles, mineral particles, mesoporous molecular sieves and commercially available absorbent particles. More preferably, it is further possible to use an absorbent selected from the group consisting of synthetic/natural polymer particles such as polyethylene particles,

polypropylene particles, polystyrene particles, polyurethane particles, pulp, cellulose particles, cork particles and wood powder; mineral particles having phyllosilicate structures such as clay, paragonite, montmorillonite and mica; synthetic oxide particles such as zeolite, porous silica and porous alumina; and mesoporous molecular sieves such as MCM-41 and MCM-48 made of oxide such as silica/polymer substance and having a pore diameter in 2 to 30 nm (manufactured by Mobil company); or a mixture of one or two or more selected from the group consisting of commercially available absorbents such as Absorbent W Product (manufactured by Absorption Corp.), Oclansorb (manufactured by Hi Point Industries), PP Spillover spill control (manufactured by Aldrich company) and Leak-Sorb spill absorbent (manufactured by Aldrich company). The absorbent may be used in the form of a mixture wherein two or more absorbents selected from the above mentioned absorbents are combined.

As absorbents in the present invention, inorganic materials such as minerals are more preferable than organic materials such as polymers.

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Inorganic absorbents such as minerals have better mechanical, thermal and electrochemical stability as compared to organic absorbents such as porous polymers, and thus the performance of the rechargeable cells utilizing inorganic absorbents is better than that of the rechargeable cells utilizing organic absorbents. Namely, it was found that when the cells are fabricated by assembling a cathode and an anode by means of pressing or lamination method, the organic

absorbents differ from the electrolyte films or polymer binders of composite electrodes in their mechanical and thermal behaviors, and thus the rechargeable cells utilizing these organic absorbents show significant reduction in their discharge capacity during repeated charge and discharge as compared to the rechargeable cells utilizing inorganic absorbents. For example, absorbents consisting of organic materials such as polymers with low melting points or deteriorating mechanical strength may lose their absorption ability in the course of pressing or lamination procedures. In other words, the use of organic absorbents such as polymers may be beneficial to the performance of electrolyte films or solid electrolytes themselves, but it may be very difficult to maintain their original performance when electrochemical cells are fabricated by means of the pressing or lamination method.

In addition, as explained above, since the ionic conductivity in general polymer electrolytes is directly affected by the movement of polymer chains, the effect of temperature on ionic conductivity becomes significant. Particularly, at low temperatures, the movement of polymer chains is weakened, which significantly reduces the ionic conductivity, thereby resulting in severe deterioration in the performance of the cells. However, the use of inorganic absorbents increases the ionic conductivity. Moreover, if a large amount of inorganic absorbent, which is less affected by temperature, is used, the effect of temperature becomes less unlike the properties of general polymer electrolytes. As a large amount of inorganic absorbent is contained in electrolytes, the electrolytes have some merits in that the resistance against ignition or explosion is improved as compared to the

electrolytes containing a large amount of organic material such as polymers.

Accordingly, it can be confirmed that it is preferable to use
5 inorganic absorbents rather than use organic absorbents in the constitution of the electrolyte film of rechargeable cells.

The amount of absorbents added is 30 to 95 % by weight and preferably, 50 to 90 % by weight based on the weight of the dried state
10 electrolyte film that does not contain liquid electrolyte. If the added amount exceeds 95 % by weight, the mechanical strength of the electrolyte film formed falls. If the amount is not more than 30 % by weight, the ability to absorb liquid electrolyte decreases. The particle size of absorbents is preferably not more than 40 μm , more preferably,
15 not more than 20 μm so as not to decrease the mechanical strength and the uniformity of the electrolyte film.

As polymer binders, most common polymers can be used. Among them, it is preferred to use a mixture of one or two or more
20 polymers selected from the group consisting of copolymers of polyvinylidene fluoride, vinylidene fluoride and hexafluoropropylene, copolymers of vinylidene fluoride and maleic anhydride, polyvinylchloride, polymethylmethacrylate, polymethacrylate, cellulose triacetate, polyurethane, polysulfone, polyether, polyolefine
25 such as polyethylene or polypropylene, polyethylene oxide, polyisobutylene, polybutyldiene, polyvinylalcohol, polyacrylonitrile, polyimide, polyvinyl formal, acrylonitrilebutyldiene rubber,

ethylene-propylene-diene-monomer, tetra(ethylene glycol)diacrylate, polydimethylsiloxane, polycarbonate and polysilicon, or copolymers thereof.

5 As solvents for dissolving polymer binders, a mixture of one or two or more solvents selected from the group consisting of N-methylpyrrolidinone, dimethylformamide, dimethylacetamide, tetrahydrofuran, acetonitrile, cyclohexanone, chloroform, dichloromethane, hexamethylphosphoramide, dimehtylsulfoxide,
10 acetone and dioxane can be used.

The liquid electrolytes, which are to be absorbed in electrolyte film containing absorbents, can be prepared by dissolving lithium salt in an organic solvent. In the present invention, the absorption of the
15 liquid electrolytes into electrolyte film is defined as "activation".

It is preferred that said organic solvents have high polarity and no reactivity to lithium metal so as to improve the degree of dissociation of ions by raising the polarity of electrolyte and to
20 facilitate ion conduction by lowering local viscosity around ions. Examples of such organic solvents include ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, γ -butyrolactone, dimethylsulfoxide, 1,3-dioxane, tetrahydrofuran, 2-methyltetrahydrofuran, sulfolane, N,N-
25 dimethylformamide, diglyme, triglyme and tetraglyme. In particular, it is preferred that the organic solvent is used in the form of mixed

solutions of two or more solvents consisting of high viscosity solvents and low viscosity solvents.

Said lithium salt is preferred to have low lattice energy and a high degree of dissociation. Examples of such lithium salt include mixtures of one or two or more selected from the group consisting of LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , LiSCN , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$. The concentration of the lithium salt is preferably 0.5M to 2M.

The liquid electrolyte can be added in an amount of 30 to 90 % by weight, preferably 40 to 85 % by weight, based on the total amount of electrolytes including the liquid electrolyte.

The solid electrolyte according to the present invention is characterized by the facts that it is easy to prepare when compared to prior polymer electrolytes; that it has higher ionic conductivity because the conduction of lithium ions proceeds via liquid phase; and that it is not affected by moisture or temperature until it absorbs the liquid electrolyte or it is activated.

The present invention also relates to a method for the preparation of the solid electrolyte.

The solid electrolyte according to the present invention can be prepared by four steps, i.e., mixing an absorbent with a polymer binder, dissolution of the resulting mixture, casting (and drying) and activation.

By passing through said mixing, dissolution and casting (and drying) steps, an electrolyte film in a dried and solid state can be obtained, which is then subjected to activation step by absorbing the liquid electrolyte.

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Namely, a mixture of the absorbent and the polymer binder is dissolved in a solvent for the polymer binder and then the resulting solution is molded into a film form and dried to form an electrolyte film with thickness of 10 to 200 μm . To the electrolyte film in a dried state an ion conductive liquid electrolyte to be absorbed is introduced, resulting in a solid electrolyte according to the present invention.

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In the following, the method for preparing the solid electrolyte is explained in greater detail.

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First of all, an absorbent in powder form (particle size of not more than 40 μm) and a polymer binder are dry mixed in a closed container.

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Both the absorbent and the polymer binder are dissolved in a solvent for the polymer binder. The solid content of said mixed solution is preferably 5 to 50 % by weight based on the total weight of the solution. If the content is less than 5 % by weight, the mechanical strength of the electrolyte film falls and if the content is more than 50 % by weight, the polymer binder cannot be dissolved sufficiently or the viscosity of the mixed solution becomes large, which is problematic.

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In order to facilitate the dissolution of the polymer binder and to avoid the agglomeration between absorbent, a magnetic stirrer, a mechanical stirrer, a planetary mixer or a high-speed disperser can be adopted to stir the mixed solution. While stirring, an ultrasonic stirrer
5 may be used to prevent the absorbent from agglomerating or foaming in the middle of mixing. In addition, if desired, the mixed solution may be subjected to defoaming and filtration steps.

After the polymer binder is completely dissolved and uniformly
10 mixed with the absorbent, the resulting mixture is molded in the form of film with a regular thickness. For example, the mixed solution may be poured on a flat glass plate or a Teflon plate and then be subjected to casting so that the resulting products have a regular thickness. Alternatively, the mixed solution may be extracted from a die with a
15 regular space and then coated onto a substrate made of polymer film. Various other application methods can be selected. It is preferred that the thickness of the film be controlled in the range of 10 to 200 μm . If the thickness of the film is not more than 10 μm , the mechanical strength will weaken, and if the thickness of the film exceeds 200 μm ,
20 the ionic conductivity decreases, which is not preferable.

After completely drying the resulting film, the liquid electrolyte is introduced thereto.

25 The present invention is directed to rechargeable cells, particularly to lithium rechargeable cells wherein said solid electrolyte is used as an electrolyte.

In one embodiment of the method for the production of rechargeable cells by the use of the solid electrolyte according to the present invention, a cell can be constructed by bonding a cathode and an anode, interposed with the electrolyte film prepared from the above-mentioned procedure. The electrolyte film contains the absorbent powder therein; the cathode is electrically connected to a cathode current collector; and the anode is electrically connected to an anode current collector. Thus the constructed assembly is activated to be able to absorb the liquid electrolyte, thereby obtaining electrochemical cell which is ready to operate.

Fig. 1 illustrates a cross sectional view of the rechargeable cell in which the solid electrolyte according to the present invention is used. The solid electrolyte (1) contains the absorbent powder (11) and the liquid electrolyte, which is absorbed during the activation step. The cathode (2) is electrically connected to a cathode current collector (22) and the anode (3) is electrically connected to an anode current collector (33), respectively.

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The procedures for the preparation of the cathode or anode are as follows. The cathode or anode consists of a current collector and an active material layer. The active material layer comprises of active materials, conducting materials and binder, etc. Besides, various additives may be introduced in order to improve the performance of cells. The current collectors, conducting materials, binders and

additives, which are contained in the cathode or anode, may be identical or different, depending on desired intentions.

The current collectors provide mobile pathways for electrons, which are generated in the oxidation/reduction reaction, taking place in the cathode or the anode. As current collectors, generally grids, foils, punching foils and etching foils, etc., may be used, depending on the performance or manufacturing processes of the cell. The use of grids can increase the filling rate of the active material, but it may complicate the manufacturing process. The use of foils can improve the performance of the cell and simplify the manufacturing process, but it may deteriorate the filling rate of the active materials. Copper, aluminum, nickel, titanium, stainless steel, carbon, etc., can be used as current collectors. Generally, aluminum is used for the cathode and copper is used for the anode.

The active materials are the most crucial component of cells since they determine the performance of cells in view of the fact that the charge and discharge reaction (or oxidation/reduction reaction) of cells take place on these materials. Furthermore, the active materials possess the largest content in the active material layer. As cathode active materials, it is possible to use oxide compounds or sulfide of transition metals, organic compounds, polymer compounds, etc. Preferably, it is possible to use oxide compounds or polymer materials such as lithium cobalt oxide (Li_xCoO_2), lithium nickel oxide (Li_xNiO_2), lithium nickel cobalt oxide ($\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$), spinel type lithium manganese oxide ($\text{Li}_x\text{Mn}_2\text{O}_4$), manganese dioxide (MnO_2), etc. As

anode active materials, alkali metals, alkali earth metals, carbon, oxide compounds or sulfide compound of transition metals, organic compounds and polymer compounds may be used, preferably carbon or polymer materials can be used. It is essential that the active materials should be chosen in accordance with the desired performance or use of electrochemical cells.

The conducting materials refer to materials that are added to the cathode or anode in order to improve the electronic conductivity, and are generally carbon. Among them, conducting materials are preferably graphite, cokes, activated carbon and carbon black, more preferably graphite and carbon black. One or two or more of conducting materials selected from the above group can be used and there is no difference whether they are synthetic or natural materials. The conducting materials are added in an amount of 3 to 15 % by weight based on the total weight of the electrode materials. If the amount of the conducting materials added is not more than 3 % by weight, the electrical conductivity decreases, causing the problem of over potential. If the amount exceeds 15% by weight, the energy density per unit volume decreases and the side reaction due to the conducting materials become severe.

The binders refer to components to be added to increase the binding ability of the active materials and are generally polymer compounds. The polymer compounds that are used in the preparation of the solid electrolyte film may serve as binders. It is preferable to use binders, which are the same as polymers of the electrolyte film or have

miscibility. The binders may be added in an amount of 15 % by weight based on the total weight of the electrode materials. If the amount of binders is less than required, the binding ability of the electrodes may decrease. If the amount of binders exceeds 15 % by weight, the processability and porosity of the electrodes decrease.

The additives refer to materials, which are added to improve the performance of cells or electrodes and can be chosen within a wide range in accordance with desired performances or use. The additives are added to improve the binding ability with composite electrode inside or current collectors, to induce the porosity or non-crystallinity of the composite electrode, to improve the dispersibility of the composite electrode constituting materials or the efficiency of the process for the manufacturing of the electrodes, to prohibit the overcharge/overdischarge of the active materials, to recombine or remove the side reaction products, or to improve the absorption ability of the liquid electrolytes. Generally, salts, organic/inorganic compounds, minerals and polymer compounds can be used as additives, and absorbents added to the electrolyte film can be chosen.

In the following, the rechargeable lithium cell according to the present invention will be explained in greater detail.

First, a mixture of an absorbent and a polymer binder is dissolved in a solvent for polymer binders to form a solution, which is made into a film and then the resulting film is dried to form an electrolyte film with a thickness of 10 to 200 μm . The obtained

electrolyte film is assembled with a cathode and an anode prepared separately to form an electrochemical cell, to which a liquid electrolyte is absorbed to obtain the rechargeable lithium cell. The solid electrolyte should be subjected to an activation step absorbing the liquid
5 electrolyte in order to have a sufficient ionic conductivity for being used. By passing through the activation step, the solid electrolyte comes to be workable as an electrochemical cell. In case that the solid electrolyte fails to pass through the activation step, the ionic conductivity at room temperature decreases drastically, which renders
10 the solid electrolyte itself inappropriate as an electrolyte.

The process for the preparation of the cathode and/or anode to be assembled with said electrolyte film is as follows. Each mixture of the cathode or anode materials is kneaded to give slurry. The resulting
15 slurry is molded to a thin film by means of casting, coating and screen printing and then the resulting thin film is combined with a current collector by means of pressing or lamination to form a cathode and/or an anode. Alternatively, the slurry may be directly coated on a current collector to form a cathode and/or an anode.

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Onto the surface of the electrodes manufactured by the above-mentioned methods, a solid electrolyte slurry consisting of an absorbent, a polymer binder and a solvent may be directly applied to form a cell in which an electrolyte film is formed on the electrodes.
25 Alternatively, one may constitute a cell by lamination or pressing the separately manufactured electrodes and electrolyte film. When a cell is constructed by the former method, the binding ability between the

electrodes and the electrolyte film may increase. However, it will be hard to adopt the former method when the electrodes and the electrolyte film do not correspond with each other, or when the electrodes or the electrolyte film are easy to pollute or lose their performance in the course of manufacturing process. In the latter method, although there is a demerit in that the binding ability between the electrodes and the electrolyte film is weak, there are much better merits in that it simplifies the quality control, process design and equipment used. Therefore, the latter method is preferred to the former one.

The electrolyte film prepared by the present invention contains an absorbent and thus has advantages in that it has higher mechanical strength as compared to pure electrolyte films or other electrolyte films containing gel type polymer electrolytes or plasticizers. Accordingly, because the electrolyte film of the present invention shows little change in its shape during the pressing or lamination procedure and has high reproducibility, it has merits in that it can be produced with a low failure rate and on a large scale. Namely, it can be stated that the electrolyte film prepared by the present invention has properties suitable for pressing or lamination methods, which are more advantageous in terms of quality control, process design and equipment used.

25

Brief Description of Drawings

Figure 1 is a cross sectional view of the cell wherein the solid electrolyte according to the present invention is used.

Figure 2 shows graphs demonstrating the experimental results of linear sweep voltammetry to determine the electrochemical stability of the solid electrolyte according to the present invention.

Figure 3 shows a variation of discharge capacity of the cell in which the solid electrolyte containing an inorganic absorbent is used as compared to the cell in which polymer absorbent is used with repeated charge and discharge.

Drawing Reference Numerals:

- | | |
|----------------------|-------------------------------|
| 1: solid electrolyte | 11: absorbent powder |
| 2: cathode | 22: cathode current collector |
| 3: anode | 33: anode current collector |

Best Mode for Carrying out the Invention

In the present invention, the solid electrolyte containing absorbents according to the present invention and the process for the preparation of cells by using said solid electrolyte are explained in detail. Firstly, the production of the solid electrolyte and the examination of performances were carried out. In addition, the solid electrolyte is assembled together with the cathode and anode to form a cell and then the procedure to examine the performance of the cell is described. However, the present invention is not restricted to those

examples and various modifications are possible within the scope of the invention.

Example 1

5 An absorbent and a binder powder were introduced to a 20 ml vial and then dry mixed for approximately 5 minutes with a magnetic stirrer. To the resulting mixture 4 ml of N-methyl pyrrolidinone was added and then continuously stirred until the binder was completely dissolved. In order to prohibit the absorbent particles from agglomerating with each other, the resulting solution was further subjected to ultrasonic stirring for 30 minutes while stirring. The mixed solution thus prepared was coated onto a glass plate in thickness of 100 μm , dried at room temperature for 2 hours or so and then further dried for 6 hours in a vacuum drier. The temperature in the vacuum drier was controlled to approximately 50°C. The electrolyte film thus prepared was soaked in a liquid electrolyte solution for approximately 10 minutes. After the liquid electrolyte was completely absorbed, the weight change was determined. The ionic conductivity was also determined by the use of an alternate current impedance method.

Table 1 summarizes the kinds of absorbents and binders, the properties of the solid electrolyte in accordance with its content and conductivity. In order to compare the ability of electrolyte film absorbing the liquid electrolyte, sorption capacity (Δ_{ab}) was defined as follows:

Δ_{ab} = [amount of the liquid electrolyte absorbed (mg)]/[weight of the electrolyte film (mg)]

Publ. No. 2000/000000

Table 1

E x.	Absorbents		Binder		Liquid Electrolyte	Δ_{ab}	Ionic Conduc tivity mS/cm	Mechanical strength
	Kind	g	Kind	g				
a	Paragonite	0.13	PVdF	0.28	EC/PC 1M LiPF ₆	0.5	0.01	Very Good
b	Paragonite	0.17	PVdF	0.26	EC/PC 1M LiPF ₆	0.7	0.02	Very Good
c	Paragonite	0.72	PVdF	0.24	EC/PC 1M LiPF ₆	0.9	0.17	Very Good
d	Paragonite	1.06	PVdF	0.26	EC/PC 1M LiPF ₆	1.5	0.19	Good
e	Paragonite	1.51	PVdF	0.25	EC/PC 1M LiPF ₆	2.2	0.39	Good
f	Paragonite	2.00	PVdF	0.26	EC/PC 1M LiPF ₆	5.0	0.63	Good
g	Paragonite	1.98	PVdF	0.25	EC/DMC 1M LiPF ₆	5.5	0.75	Satisfactory
h	Zeolite	1.37	PVdF	0.60	EC/DMC 1M LiPF ₆	4.7	0.68	Good
i	Zeolite	1.50	PVdF	0.38	EC/DMC 1M LiPF ₆	5.5	0.85	Good
j	Zeolite	1.65	PVdF	0.29	EC/DMC 1M LiPF ₆	5.8	0.91	Satisfactory
k	Montmoril lonite	1.34	PVdF	0.58	EC/DMC 1M LiPF ₆	4.4	0.70	Good
l	Montmoril lonite	1.50	PVdF	0.38	EC/DMC 1M LiPF ₆	5.8	0.82	Good
m	Silica	1.35	PVdF	0.59	EC/DMC 1M LiPF ₆	5.6	0.75	Good
n	Polypropyl ene	1.35	PVdF	0.60	EC/DMC 1M LiPF ₆	5.7	0.80	Good
o	Wood powder	1.35	PVdF	0.60	EC/DMC 1M LiPF ₆	5.5	0.79	Good
p	Paragonite	2.00	P(VdF -HFP)	0.26	EC/DMC 1M LiPF ₆	5.1	0.76	Good
q	Paragonite	1.95	PAN	0.25	EC/DMC 1M LiPF ₆	5.0	0.74	Good
r	Paragonite	2.00	PU	0.26	EC/DMC 1M LiPF ₆	5.3	0.72	Good
s	Paragonite	1.98	PVC	0.25	EC/DMC 1M LiPF ₆	5.5	0.78	Good
t	Paragonite	2.00	P(VdF -HFP)	0.26	EC/DMC 1M LiPF ₆	5.4	0.75	Good
u	Zeolite	2.00	P(VdF -HFP)	0.26	EC/DMC 1M LiPF ₆	5.3	0.78	Good
v	Zeolite	1.95	PAN	0.25	EC/DMC 1M LiPF ₆	5.1	0.74	Satisfactory
w	Zeolite	2.00	PU	0.26	EC/DMC 1M LiPF ₆	5.2	0.72	Good
x	Zeolite	1.98	PVC	0.25	EC/DMC 1M LiPF ₆	5.4	0.78	Good
y	Zeolite	2.00	P(VdF -HFP)	0.26	EC/DMC 1M LiPF ₆	5.3	0.75	Good

Example 2 (Comparative Example)

The same procedure as in Example 1-(f) was repeated to form an electrolyte film except that no absorbent was added in order to determine the effect of absorbents on the electrolyte film prepared. The electrolyte film prepared was transparent and had good mechanical strength. However, when the electrolyte film thus prepared was soaked in a liquid electrolyte solution at room temperature for 10 hours, the weight of the electrolyte film before and after the soaking was almost the same within measurement error. In addition, the ionic conductivity of the solid electrolyte thus prepared could not be measured by means of an alternate current impedance method.

Example 3

In order to determine the electrochemical stability of the solid electrolyte containing absorbents, the linear sweep voltammetry method was carried out by the use of a stainless steel (#304) as an operating electrode and lithium metal as an opposite electrode and a standard electrode. The electrochemical voltage applied in the linear sweep voltammetry was from an open circuit voltage to 5.4 V (vs. Li/Li^+). The scan rate of the linear sweep voltammetry was 10 mV/sec. The results of the linear sweep voltammetry measured on the solid electrolyte prepared by the methods of Example 1-(g), 1-(i) and 1-(l) are shown as A, B and C, respectively, in Fig. 2.

Example 4

In order to determine the performances of the cell using the solid electrolyte containing inorganic absorbent, an oxide compound cathode, a carbon anode and a solid electrolyte according to the present invention were assembled to fabricate cells, and then the charge and discharge test on thus fabricated cells was carried out. The fabricated cells were in a laminated form and were prepared by lamination of the cathode, anode and electrolyte film to form an assembly, to which a liquid electrolyte was absorbed. The constant current was applied with a rate charging the reversible capacity within 2 hours (C/2 rate) until the cell voltage became 4.2 V, and then the constant voltage of 4.2 V was applied again until the current decreased down to C/10 mA. Subsequently, the discharging current was applied with a rate discharging the voltage down to 2.5 V or 2.75 V within 2 hours (C/2 rate). The charge and discharge experiment was repeated and the change of discharge capacity with the charge and discharge was measured. The cell constitution and the test results are summarized in the following Table 2 and shown in Fig. 3. As listed in Table 2, the solid electrolyte refers to the conditions where a liquid electrolyte is absorbed into an electrolyte film.

Table 2

Ex.	Cathode				Anode				Solid Electrolyte	Fig.
	Active material	Conducting material	Binder	Additive	Active material	Conducting material	Binder	additive		
z	LiCoO ₂	carbon black	PVdF	Zeolite	graphite	carbon black	PVdF	zeolite	Ex. 1-(f)	Fig. 3-D
aa	LiCoO ₂	carbon black	PVdF	Zeolite	graphite	carbon black	PVdF	zeolite	Ex. 1-(g)	Fig. 3-E
bb	LiCoO ₂	carbon black	PVdF	Zeolite	graphite	carbon black	PVdF	zeolite	Ex. 1-(n)	Fig. 3-F
cc	LiCoO ₂	carbon black	PU	Zeolite	graphite	carbon black	PU	zeolite	Ex. 1-(r)	Fig. 3-G
dd	LiMn ₂ O ₄	carbon black	P(VdF-HFP)	Zeolite	graphite	carbon black	P(VdF-HFP)	zeolite	Ex. 1-(u)	Fig. 3-H

Fig.3 illustrates the discharge capacity with repeated charge and discharge of the cell obtained by the respective examples in comparison with the first discharge capacity. From the test results, it was confirmed that the use of the solid electrolytes containing inorganic absorbents (Examples 4-z, aa, cc, dd) shows much better cell performance than that of the solid electrolyte containing organic absorbents (polymer) (Example 4-bb). Namely, the solid electrolyte containing inorganic absorbent has a much better effect on the total cell performance (charge and discharge performance, etc.), although the electrolyte film or solid electrolyte itself does not show any significant differences in properties (ionic conductivity, mechanical strength, etc.).

Industrial Applicability

As it can be understood from the above descriptions, the solid electrolytes containing absorbents according to the present invention are characterized by the following facts:

they have high mechanical strength, which makes them suitable to be made into thin films;

they have high ionic conductivity corresponding to that of the liquid electrolytes;

unlike general polymer electrolytes in gel type, they do not require any particular dehumidifying atmosphere since lithium salt, which is easily decomposed by a trace amount of moisture, is not introduced during the manufacturing of the electrolyte films;

they have a broad electrochemical potential window since the absorbent therein is electrochemically stable; and

they are of ease in automation for mass production due to the simple process for the production of the electrolyte.

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In addition, it is possible to minimize the surface resistance between the electrolyte and electrodes since the binding ability with the cathode and anode is excellent and the volume change due to the introduction of the liquid electrolyte is little. The solid electrolytes containing inorganic absorbents also show superior mechanical, thermal and electrochemical stability to those of the solid electrolytes containing organic absorbents, thereby showing less decrease in their discharge capacity during the repeated charge and discharge, which makes it suitable for being used as an electrolyte for rechargeable lithium cells.

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